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# Pull-out simulations of a capped carbon nanotube in carbon nanotube-reinforced nanocomposites

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Systematic atomic simulations based on molecular mechanics were conducted to investigate the pull-out behavior of a capped carbon nanotube (CNT) in CNT-reinforced nanocomposites. Two common cases were studied: the pull-out of a complete CNT from a polymer matrix in a CNT/polymer nanocomposite and the pull-out of the broken outer walls of a CNT from the intact inner walls (i.e., the sword-in-sheath mode) in a CNT/alumina nanocomposite. By analyzing the obtained relationship between the energy increment (i.e., the difference in the potential energy between two consecutive pull-out steps) and the pull-out displacement, a set of simple empirical formulas based on the nanotube diameter was developed to predict the corresponding pull-out force. The predictions from these formulas are quite consistent with the experimental results. Moreover, the much higher pull-out force for a capped CNT than that of the corresponding open-ended CNT implies a significant contribution from the CNT cap to the interfacial properties of the CNT-reinforced nanocomposites. This finding provides a valuable insight for designing nanocomposites with desirable mechanical properties. © 2013 AIP Publishing LLC.

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## I. INTRODUCTION

To date, many experiments have demonstrated that the pull-out of a carbon nanotube (CNT) is a common critical phenomenon, as seen from the observation of fracture surfaces of CNT-reinforced nanocomposites.<sup>1–5</sup> The observed CNT pull-out behavior can be divided into the following two categories: the pull-out of a complete CNT from a matrix<sup>1–3</sup> and the pull-out of the broken outer walls of a CNT from the intact inner walls embedded in a matrix (i.e., the so-called sword-in-sheath mode).<sup>4,5</sup> The decrease in the load-carrying capability of CNT-reinforced nanocomposites due to this CNT pull-out behavior may be detrimental to the overall mechanical properties of bulk nanocomposites, such as stiffness and strength.<sup>6</sup> Thus, the continuously increasing demand for the development of nanocomposites with significant mechanical properties has led to thorough investigations of this pull-out behavior, with the goal of finding effective strategies to enhance the interfacial properties between CNTs and matrices, and therefore improve the desirable overall mechanical properties.

Direct pull-out experiments have been performed to evaluate the interfacial shear strength of CNT-reinforced nanocomposites.<sup>7–11</sup> The measured pull-out force was divided by the embedded lateral area of the CNT. Various theoretical models based on continuum mechanics have also been developed to predict the interfacial shear strength.<sup>12,13</sup>

Moreover, atomic simulations<sup>14,15</sup> have provided an alternative method to predict the interfacial shear strength by analyzing the variation in the potential energy.

However, to the best of our knowledge, no direct quantitative comparison between numerically predicted pull-out forces and experimental data has been reported because the existing numerical values are generally much lower (from at least ten to several hundred times lower) than the reported experimental data. Moreover, there is no systematic study regarding the effect of a CNT's unique capped structure on the pull-out behavior of CNT in nanocomposites, although this cap has a significant influence on the pull-out of the outer walls against the inner walls in a multi-walled carbon nanotube (MWCNT) (i.e., interfacial sliding between the nested walls in an MWCNT).<sup>16–21</sup> It should be noted that the pull-out force of the outer walls against the inner walls in an MWCNT itself generally consists of the van der Waals (vdW) force and the frictional force between the walls. The frictional force may be significant when referring to the defects or chemical cross-linking.<sup>17–19</sup> However, for CNTs with a high crystallinity, the vdW force should be dominant. In our previous experimental and computational study,<sup>21</sup> the frictional effect between the walls was determined to be very small because of the high crystal quality of the nearly defect-free MWCNT. A similar issue also occurs in the pull-out of CNTs from various matrices.

We have previously simulated the pull-out process of an open-ended CNT in detail using molecular mechanics (MM) for CNT/polymer<sup>14</sup> and CNT/alumina<sup>15</sup> nanocomposites. As

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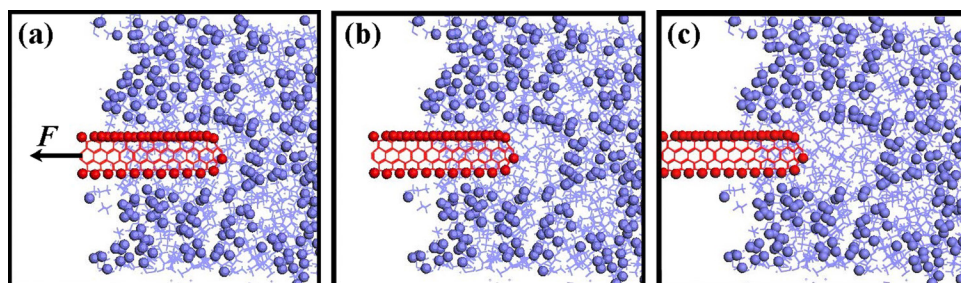


FIG. 1. Pull-out process of an SWCNT (5,5) from a PE matrix.

a continuation of those work, here, we investigated the pull-out behavior of a capped CNT in the same two nanocomposites for the first time. Because we focused on the effect of the CNT cap on the pull-out behavior, the interfacial region between the CNT and the polymer or alumina matrix was assumed to be perfect, having only vdW interactions and neglecting possible interfacial defects, chemical bonding, and mechanical cross-links. By conducting a series of MM pull-out simulations, detailed information on the energy difference between two consecutive pull-out steps (i.e., energy increment) during the pull-out process was obtained. On this basis, a set of empirical formulas was created to predict the corresponding pull-out force, and the predictions from these formulas were quite consistent with previous experimental measurements.

## II. PULL-OUT OF A COMPLETE CAPPED CNT IN CNT/POLYMER NANOCOMPOSITES

The pull-out of complete CNTs from various polymer matrices has been clearly observed in the fracture surfaces of various CNT/polymer nanocomposites,<sup>1–3</sup> which may imply comparatively weak interface between the CNT and the surrounding polymer matrix. To understand the inherent characteristics of this pull-out behavior, we analyzed the pull-out process of an open-ended CNT from a polyethylene (PE) matrix in detail in our previous work.<sup>14</sup> It was concluded that the corresponding pull-out force is independent of the nanotube length and the nanotube chirality, but it is proportional to the nanotube diameter. Moreover, we demonstrated<sup>20,21</sup> that the capped structure of the CNT significantly affects the pull-out behavior of the outer walls against the inner walls in an MWCNT in the sword-in-sheath mode, based on an extensive quantitative comparison between the MM simulation results and the experimental data.

Based on the above outcomes, the effect of the cap on the CNT pull-out behavior from the polymer matrix was investigated as below. Three capped, single-walled carbon nanotubes (i.e., SWCNT (5,5), (10,10), and (12,12)), each with the same length of 2.46 nm but with different diameters, were incorporated into a PE matrix. The construction of the simulation cell is described in detail elsewhere.<sup>14</sup>

The pull-out simulations of the three capped SWCNTs based on MM were conducted in a manner similar to those in our previous work.<sup>14,15</sup> The pull-out process of the capped SWCNT (5,5) is schematically described in Fig. 1 as a representative example where a prescribed displacement of the CNT is applied in its axial direction. Note that to evaluate the difference in the potential energy between two consecutive pull-out steps, i.e., the energy increment  $\Delta E$ , a much smaller displacement increment ( $\Delta x = 0.01$  nm) than the 0.2 nm used in the previous simulations<sup>14</sup> was used in the present simulation to explore the cap effect in a more detailed way. It should be noted that the quasi-static characteristics of the present MM simulations yielded a considerable improvement in the computational efficiency compared with that of traditional molecular dynamics (MD) simulations because the velocity components of the individual atoms within the system are ignored. In other words, the MM method is insensitive to the effects of thermal instability and kinetic excitation, and can therefore be reasonably expected to provide an accurate representation of the deformation with a low strain rate in the nanomaterial.

The obtained variations in the energy increment  $\Delta E$  during the pull-out process for the three SWCNTs with different nanotube diameters  $D_o$  are shown in Fig. 2(a). It can be observed that for each SWCNT, the energy increment  $\Delta E$  increases rapidly to a peak value at a specified displacement (labeled stage-1 in Fig. 2(a)) then remains steady as the pull-out continues (labeled stage-2 in Fig. 2(a)). Finally,  $\Delta E$

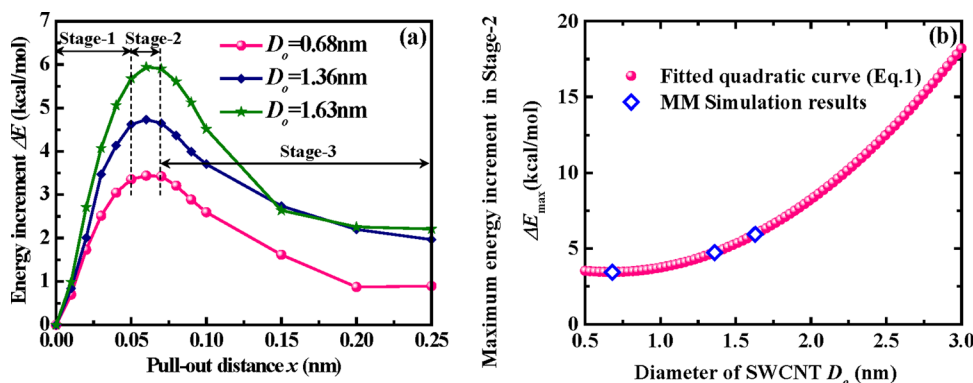


FIG. 2. Energy increment during pull-out of an SWCNT from a PE matrix. (a) Energy increment  $\Delta E$  versus pull-out displacement  $x$ ; (b) maximum energy increment  $\Delta E_{\max}$  versus nanotube diameter  $D_o$ .



decreases quickly and reaches a comparatively flat stage (labeled stage-3 in Fig. 2(a)). After entering stage-3, to reduce the computational cost, the simulation is stopped without further pull-out once the energy increment becomes stable. This energy increment ( $\Delta E$ ) profile is surprisingly consistent with that of the pull-out of the outer walls from the inner walls in a capped MWCNT obtained numerically<sup>21</sup> or experimentally.<sup>22–24</sup> The results are also similar to some experimental results of the pull-out forces of MWCNTs from polymer matrices.<sup>7–9</sup> Moreover, as shown in Fig. 2(a), the maximum energy increment (i.e.,  $\Delta E_{\max}$  in stage-2) increases with the nanotube diameter.

The relationship between the maximum energy increment  $\Delta E_{\max}$  and the nanotube diameter  $D_o$  can be approximated with a quadratic function (see Fig. 2(b)) as follows:

$$\Delta E_{\max} = 2.72D_o^2 - 3.65D_o + 4.67, \quad (1)$$

in which  $\Delta E_{\max}$  and  $D_o$  are in units of kcal/mol and nm, respectively. As explained for the pull-out of an outer wall from the inner wall in an MWCNT,<sup>21</sup> the reason for the quadratic increase of energy increment in Eq. (1) is that the surface energy increment of the capped area of the CNT is proportional to  $D_o^2$ . Because the energy increment is equal to the work done by the pull-out force, i.e.,  $\Delta E = F \times \Delta x$ , the maximum pull-out force in units of nN in stage-2 for the case of a capped SWCNT can be evaluated as

$$F_{\text{SWCNT}} = 1.89D_o^2 - 2.54D_o + 3.25. \quad (2)$$

For the pull-out of a complete open-ended MWCNT from a PE matrix,<sup>14</sup> it is believed that only the outer three walls have an effect on the variation in the energy increment during the pull-out process. The reason is as follows: from the outermost wall to the innermost wall, the distance between the inner walls of the CNT and the pull-out interface increases gradually. The greater the distance is, the weaker the vdW interaction. Therefore, because the cut-off distance for the vdW interaction is approximately 0.95 nm and the wall spacing of the MWCNT is 0.34 nm, the pull-out of an entire MWCNT with more than 3 walls can be simplified to that of a triple-walled carbon nanotube (TWCNT) composed of the three outermost walls of the MWCNT. From the present MM simulations, the corresponding pull-out force was found to be approximately 1.2 times that for an SWCNT composed solely of the outermost wall of the TWCNT.

On this basis, the pull-out force of a complete capped MWCNT from a PE matrix can be approximated by revising the above Eq. (2) for the pull-out force of a complete capped SWCNT as

$$F_{\text{MWCNT}} = \lambda(1.89D_o^2 - 2.54D_o + 3.25), \quad (3)$$

in which  $F_{\text{MWCNT}}$  and  $D_o$  are in units of nN and nm, respectively. Note that the coefficient  $\lambda$  indicates the effect of the wall number, which is 1.0 for an SWCNT and 1.2 for an MWCNT.

Comparisons of the numerical results for capped CNTs using the Eq. (3), the previous numerical results for

open-ended CNTs,<sup>14</sup> and the reported experimental data<sup>7–11</sup> are plotted in Fig. 3, in which the effect of the polymer matrix type in the experiments is ignored. The theoretical value,<sup>13</sup> calculated by multiplying the predicted interfacial shear strength and the embedded lateral area of CNT, was also incorporated into Fig. 3. Note that the computed interfacial shear strength<sup>13</sup> is predicted from experimental measured data using an expansion of the classical Kelly-Tyson force balance method.<sup>25</sup> In Fig. 3, the numerical pull-out force for the capped MWCNT is obviously much larger than that for the open-ended CNT.<sup>14</sup> This indicates the significant contribution of the CNT cap to the pull-out force. Moreover, it is surprising that the pull-out force predicted by Eq. (3) agrees with most of the previous experimental data very well, with the curve passing through the middle of the experimental data.

In fact, it is almost impossible to accurately match all experimental data one-by-one at the nanoscale because of the wide variety in factors such as materials, fabrication conditions, and test methods. For example, Cooper *et al.*<sup>7</sup> attempted a drag-out of an MWCNT configured to bridge a hole in a CNT/epoxy nanocomposite by loading the nanotube at its center. This setup is analogous to a cable with the two ends fixed and a center loading, and the necessary force is obviously much higher than that required for an axial pull-out. However, the pull-out force measured by Barber *et al.*<sup>8</sup> was found to be much lower than the numerical values obtained in this study. This can be explained by the sample preparation, where the CNTs were artificially pushed into the molten polyethylene-butene thin film.<sup>8</sup> Another set of pull-out tests was conducted using fractured nanocomposite specimens under tensile loading.<sup>9–11</sup>

Compared with the numerical pull-out forces obtained in this study, the slightly lower experimental results<sup>9–11</sup> may be attributed to some initial or pre-existing interface damage between the CNTs and the matrices that was induced by the tensile fracture of the nanocomposites before the pull-out of the CNTs from the matrices. As shown in Ref. 10, this initial

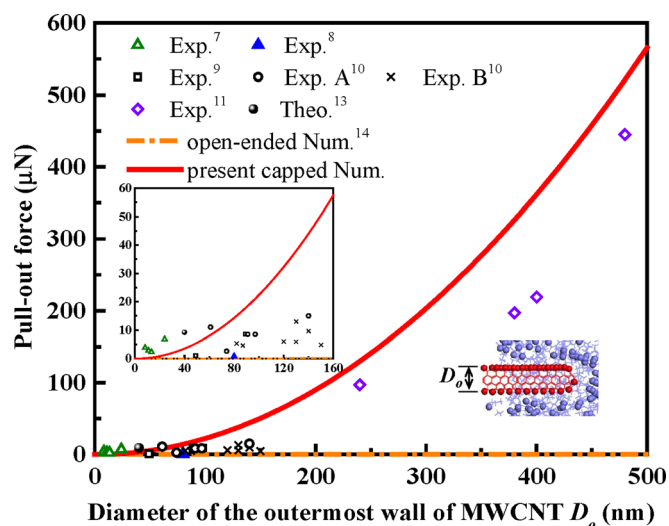


FIG. 3. Comparison of experimental,<sup>7–11</sup> theoretical,<sup>13</sup> and numerical (the previous Ref. 14 for open-ended CNTs, and the present for capped CNTs) pull-out forces in CNT/polymer nanocomposites.

interfacial damage between the CNT and a thermal plastic matrix can be partially repaired by the hot-pressing method (compare the treated specimen, exp. A<sup>10</sup> in Fig. 3, with the untreated specimen, exp. B<sup>10</sup> in Fig. 3). Therefore, the pull-out forces of exp. A<sup>10</sup> were slightly higher than those of exp. B<sup>10</sup> (see Fig. 3). Moreover, it should be noted that there is considerable data scattering, even within the same research group. This scattering is most likely due to the experimental difficulties in nano-manipulation and precise measurements.

The above comparison validates the effectiveness of the proposed empirical formulas and further highlights the significant contribution of the CNT cap to the pull-out force and the interfacial properties of a CNT/polymer nanocomposite. To explain this cap effect more clearly, as shown in Fig. 4(a), we divided an MWCNT into its cap section and its tube section for consideration. For the tube section, as shown in our previous study,<sup>15</sup> the interfacial shear stress  $\tau_i$  exists only in a small region “a” ( $=2\text{ nm}$ ) centered at the left side of the matrix because the vdW interactions in this region experience an unrecoverable breaking process. The shear stress in the overlapped region “b” in Fig. 4(a) nearly vanishes as a direct consequence of the counteraction of multiple vdW interactions  $F_{vdW}$ . During the pull-out process, repetitive breaking and reforming of the vdW interactions in this region “b” occurs and results in minor shear stresses. Therefore, the contribution of the tube section to the total pull-out force is expected to be very small.<sup>15</sup>

Moreover, as shown in Fig. 4(b), for an infinitely small region in the tube section, the relative deformation between

the CNT and the polymer matrix is in the sliding separation mode, i.e., mode-II. However, for an infinitely small region at the top of the cap, the relative deformation between the MWCNT and the polymer matrix during the pull-out process is in the opening separation mode, i.e., mode-I (see Fig. 4(c)). For these two typical deformation modes, Awasthi *et al.*<sup>26</sup> modeled an infinitely small area of an SWCNT as a piece of graphene and studied the interaction between the graphene and the PE polymer in mode-I and mode-II. They found that for the same computational system, the peak traction in mode-I is approximately 13 times greater than in mode-II. Furthermore in our previous study,<sup>21</sup> to address the pull-out of an outer wall from the inner walls in an MWCNT, two parallel, flat, monolayered graphene sheets were investigated to evaluate the potential energy variation per unit area under a specified separation displacement in mode-I and mode-II. It was found that the potential energy variation for mode-I is 3.54 times greater than that for mode-II, implying a much greater applied force required in a mode-I deformation. Therefore, all of the above evidence highlights the primary contribution of the CNT cap to the CNT pull-out behavior from a matrix, not only resulting from its large area (i.e.,  $\propto D_o^2$ ) but also from its special relative separation mode from the matrix, i.e., mode-I.

### III. PULL-OUT OF A CAPPED CNT IN SWORD-IN-SHEATH MODE IN CNT/ALUMINA NANOCOMPOSITES

It has been reported that the sword-in-sheath mode is a common fracture mode for CNT/alumina nanocomposites.<sup>4,5</sup> The detailed process as illustrated in Fig. 5, can be described as follows:<sup>5</sup> initially, tensile stress leads to crack formation in matrix and partial debonding. Then as the displacement increases, some outer walls of the MWCNT break. The intact inner walls are then pulled away, leaving fragments of the broken outer walls in the matrix (or you can say the broken outer walls are pulled away with the matrix in relatively). It should be noted that there are two pull-out interfaces, in contrast to the case of CNT/polymer nanocomposites. One

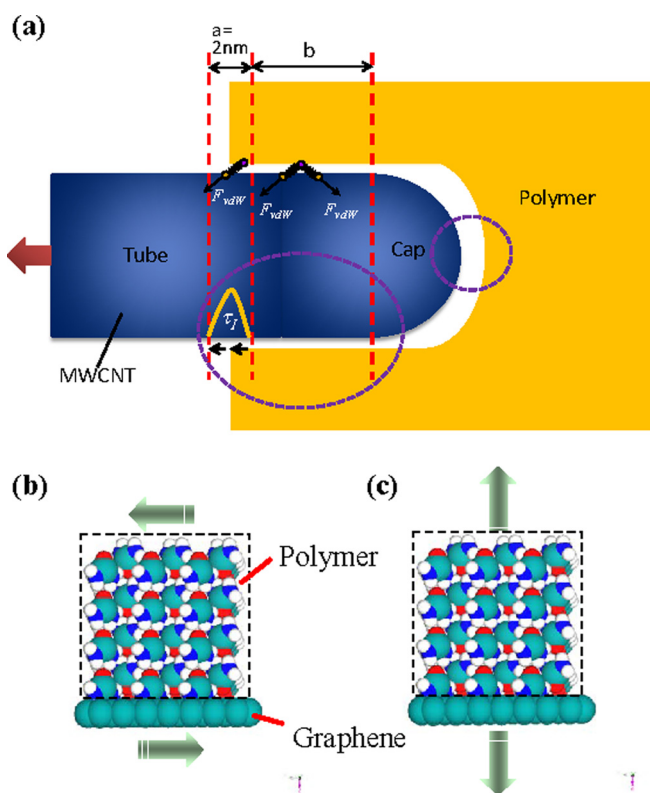


FIG. 4. Pull-out of an MWCNT from a polymer matrix and relative deformation modes in different regions. (a) Schematic of the MWCNT pull-out from the polymer matrix; (b) sliding separation mode (mode-II); and (c) opening separation mode (mode-I).

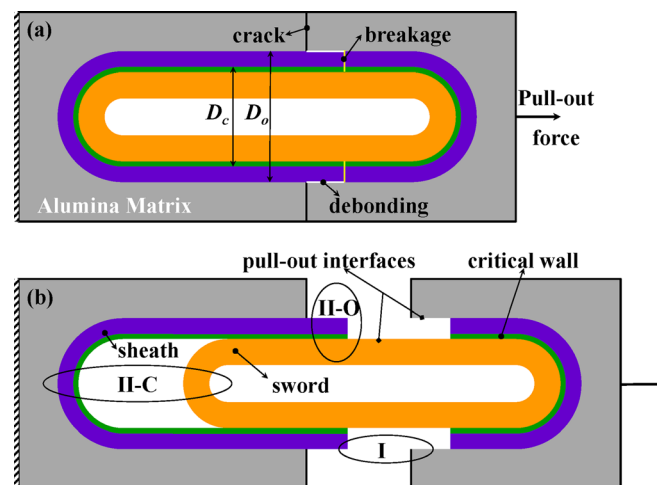


FIG. 5. Schematic of CNT pull-out with the sword-in-sheath mode in tensile tests of CNT/alumina nanocomposites.

interface is between the outermost wall and the matrix, and the other is between the nested walls in the MWCNT. This observation indicates that this pull-out behavior corresponding to the sword-in-sheath mode in CNT/alumina nanocomposites can be assumed to be the superposition of the pull-out of the broken outer walls (Fig. 5(b), I, left) from the matrix (Fig. 5(b), I, right), and the pull-out of the intact inner walls from the broken outer walls (Fig. 5(b), II, left). By further decomposing the CNT into open-ended and capped components, the pull-out between the broken outer walls and the intact inner walls (Fig. 5(b)) can be divided into the pull-out of the open-ended component (Fig. 5(b), II-O) and the pull-out of the capped component (Fig. 5(b), II-C). It should be noted that the effect of the matrix (left) on the pull-out of the broken outer walls from the intact inner walls can be ignored because the reported number of broken outer walls is approximately 10,<sup>4,5</sup> indicating a much greater distance from the matrix to the pull-out interface compared with the cut-off distance of the vdW interactions. The corresponding pull-out force for each part is discussed in the following section.

### A. (I) Pull-out of the broken outer walls from the matrix

From previous experimental observations,<sup>4,5</sup> the number of broken outer walls is usually more than 3. The model can be simplified as the pull-out of a TWCNT of diameter  $D_o$  (see Fig. 5) from the alumina matrix. For each pull-out step with a constant displacement  $\Delta x_I$  of 0.2 nm, the corresponding energy increment and the pull-out force can be predicted by<sup>15</sup>

$$\begin{aligned}\Delta E_I &= 58.26D_o + 6.50, \\ F_I &= \frac{\Delta E_I}{\Delta x_I} = 2.03D_o + 0.23.\end{aligned}\quad (4)$$

### B. (II-O) Pull-out of the open-ended component of the broken outer walls from the intact inner walls

Because the number of inner walls and outer walls is usually more than 3, the model can be simplified to the pull-out of an MWCNT with 5 walls composed of the immediate outer wall at the pull-out interface (the critical wall of diameter  $D_c$ ) in Fig. 5 and the two neighboring walls on each side.<sup>21</sup> For each pull-out step with a constant displacement  $\Delta x_{II-O}$  of 0.2 nm, the corresponding energy increment and the pull-out force can be predicted by<sup>21</sup>

$$\begin{aligned}\Delta E_{II-O} &= 37.56D_c - 10.5, \\ F_{II-O} &= \frac{\Delta E_{II-O}}{\Delta x_{II-O}} = 1.31D_c - 0.37.\end{aligned}\quad (5)$$

### C. (II-C) Pull-out of the capped component of the broken outer walls from the intact inner walls

For each pull-out step with a considerably smaller constant displacement of  $\Delta x_{II-C} = 0.01$  nm, the corresponding energy increment and the pull-out force can be predicted by<sup>21</sup>

$$\begin{aligned}\Delta E_{II-C} &= 1.29 \times (2.09D_c^2 - 2.15D_c + 0.94), \\ F_{II-C} &= \frac{\Delta E_{II-C}}{\Delta x_{II-C}} = 1.29 \times (1.45D_c^2 - 1.49D_c + 0.65).\end{aligned}\quad (6)$$

In view of the above discussions, for the pull-out of a capped MWCNT from an alumina matrix in the sword-in-sheath mode, the corresponding pull-out force can be assumed to be the sum of the above three parts (i.e., Eq. (4) for part I, Eq. (5) for part II-O, and Eq. (6) for part II-C)

$$\begin{aligned}F &= F_I + F_{II-O} + F_{II-C} \\ &= 1.87D_c^2 - 0.61D_c + 2.03D_o + 0.7.\end{aligned}\quad (7)$$

Note that the units for the diameter and the force are nm and nN, respectively.

The obtained relationship between the nanotube diameter and the predicted pull-out force is shown in Fig. 6, which indicates that the pull-out force increases with the wall diameters of both the outermost wall and the critical wall (i.e.,  $D_o$  and  $D_c$  in Fig. 5). The reason is that the numbers of atoms at both pull-out interfaces increase with the wall diameters. The larger the wall diameter is, the stronger the vdW interaction to be overcome during the pull-out. Note that the quadratic term in  $D_c$  in Eq. (7) contributed by the cap dominates the pull-out force.

The results, without considering the effect of the CNT cap, are also plotted in Fig. 6 based on the formula

$$F^* = F_I + F_{II-O} = 2.03D_o + 1.31D_c - 0.14, \quad (8)$$

where  $F^*$  is only linearly proportional to both  $D_o$  and  $D_c$ . As shown in Fig. 6, the predicted pull-out forces for capped MWCNTs are much larger than those for the corresponding open-ended MWCNTs, which indicates the significant effect of the CNT cap.

It is quite difficult to perform equivalent experiments (Fig. 5) to measure the pull-out forces to validate the

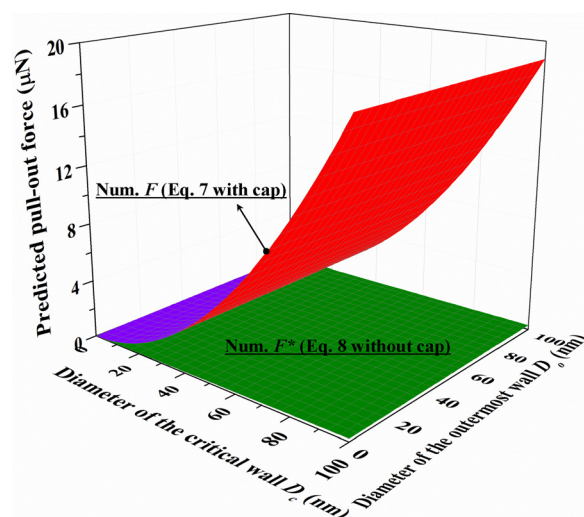


FIG. 6. Comparison of numerical pull-out forces for capped (i.e., based on Eq. (7)) and open-ended (i.e., based on Eq. (8)) CNTs in CNT/alumina nanocomposites.



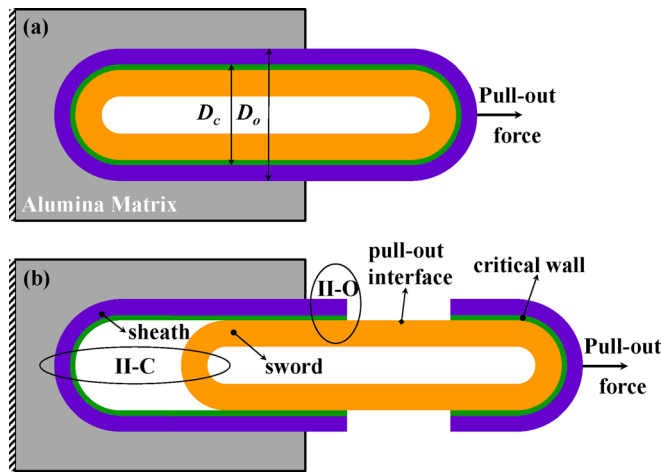


FIG. 7. Schematic of a direct CNT pull-out experiment using fractured CNT/alumina nanocomposite specimens.<sup>5</sup>

proposed formula. Nevertheless, we (see Yamamoto *et al.*<sup>5</sup>) have performed a series of MWCNT pull-out tests using an in situ SEM on fractured composite specimens while conducting bending tests. The results strongly suggested that the broken outer walls of the MWCNT and the intact inner walls are completely pulled away, leaving the companion fragments of the outer walls in the alumina matrix. This process is illustrated in Fig. 7. It can be observed that there is only one pull-out interface, in contrast to Fig. 5. Using the above method, the corresponding pull-out force should be composed only of part-II

$$F^{**} = F_{II} = F_{II-O} + F_{II-C} = 1.87D_c^2 - 0.61D_c + 0.47. \quad (9)$$

Note that both Eqs. (7) and (9) are dominated by  $D_c^2$ , and there is no significant difference between  $F$  in Eq. (7) for the problem in Fig. 5 and  $F^{**}$  in Eq. (9) for the problem in Fig. 7.

In Table I and Fig. 8, the pull-out forces predicted by Eq. (9) are compared with four experimental values<sup>5</sup> obtained by directly performing CNT pull-out tests with a CNT/alumina nanocomposite. Note that the diameter of the critical wall is calculated from the outermost wall and the number of broken walls observed in the experiments, with the assumption that the wall distance between adjacent MWCNT walls is 0.34 nm. Agreement between the experimentally measured pull-out forces and the numerical predictions was found by

TABLE I. Comparison of experimental<sup>5</sup> and numerical pull-out forces in CNT/alumina nanocomposites.

$D_o$ (nm)	Number of broken outer walls	$D_c$ (nm)	Pull-out force ( $\mu$ N)	
			Experimental <sup>5</sup>	Numerical $F^{**}$ (Eq. (9))
71	15	65.9	4.8	8.08
72	46	56.36	9.2	5.91
93	24	84.84	17.2	13.41
94	11	90.26	19.7	15.18

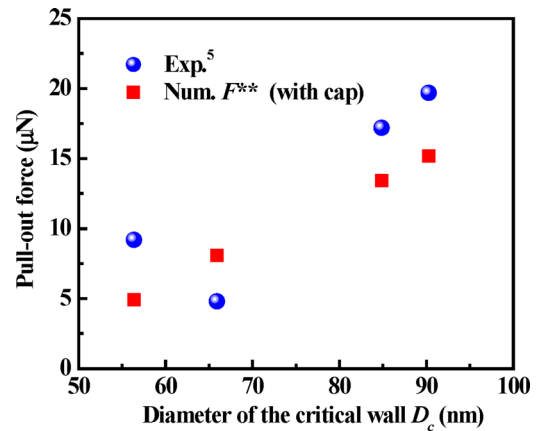


FIG. 8. Comparison of experimental<sup>5</sup> and numerical pull-out forces in CNT/alumina nanocomposites.

neglecting the wide data scattering, which is evidence of the great difficulties in nano-manipulation and obtaining precise measurements. The results suggest that the above analysis method is feasible and that the proposed empirical formula can approximately predict the pull-out force.

#### IV. CONCLUSIONS

The present work incorporates a capped CNT into a computational model for the first time to investigate its pull-out behavior in CNT-reinforced nanocomposites. Using pull-out simulations based on MM, a set of simple and empirical formulas was proposed to predict the corresponding pull-out force, which was validated by some previous experimental results. The significant contribution of the CNT cap to the pull-out force was confirmed, which deepens the understanding of the interfacial properties of CNT-reinforced nanocomposites and provides a valuable guideline to design ideal nanomaterials with desirable interfacial properties. For instance, if it is possible to synthesize dumbbell-shaped CNTs, in which there are two caps of a much larger diameter than that of the tube section, the pull-out force can be increased significantly, not only because of the contribution of  $D_o^2$  in Eq. (2) or  $(D_c)^2$  in Eq. (7) but also because of the anchor effect induced by the two caps.

It should be noted that the capped CNTs of perfect surfaces are assumed in the present models, which indicates that only vdW interactions existing between CNT and polymer matrix are contributive to the corresponding interfacial strength. That is to say, although the proposed formulas fitted from MM partially achieve great success in predicting two typical cases in Secs. II and III, they cannot be applicable everywhere or to every scale. Generally, with increasing size (e.g., for the extreme case in which the diameter are on the order of  $\mu$ m), the defects in the CNTs will certainly increase, which leads to possible mechanical cross-linking between CNTs and the matrix. Moreover, for the functionalized CNTs with wide practical application, the induced chemical bonding between CNTs and the matrix may result in further increased interfacial properties. In such above two cases or else, it is indispensable to additionally consider the effect of friction.

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